STRUCTURAL ANALYSIS OF QUINOLINE EXTRACTS AND HYDROLYSIS PRODUCTS OF COALS

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The mean structure of coals has been extensively investigated by X-ray,magnetic susceptibility,gases evolved during carbonization,IR spectra etc.,and the structural analysis was first developed by van Krevelen(1)using density and refractive index. Among these the method which gives the most precise image appears to be NMR method. However this method is limited in that it can be applied only to soluble material by special solvents. Usually coals can be dissolved only in part,therefore the results do not represent the whole coal.

Thus in the present work we tried to increase the solubility of coals using chemical reaction or strong solvent(quinoline), which would have the smallest change in the unit structure(cluster unit). The results of structural analysis of the products with these two methods are in good agreement,although both methods and their yield are quite different. This means that the structural image obtained here represents the true mean structure of coals.

Experiments

1)Coal sample. Vitrinits of 12 coal samples were concentrated using the sink and float method. Their analytical values are shown in Table 1.

2)Quinoline extraction. 5g of crushed coal under 100 Tyler mesh and 100g of purified quinoline were placed in a 500ml autoclave with a magnetic stirrer and after replacing the atmosphere by nitrogen this was heated at 350~380°C for 1~4hours. After cooling the products were centrifuged and filtered. The residue was washed with fresh quinoline and methanol. The filtrate was concentrated under vacuum and poured into 500ml of 2N HCl,filtered, washed with hot and cold water and dried.

3)NaOH-alcohol reaction(2). 5g of coal,5g of sodium hydroxide and 50g of ethyl alcohol were placed in an autoclave of 230ml with a magnetic stirrer and,after replacing the atmosphere by nitrogen,this was heated at 300°C or 350°C for 1 hour. After neutralizing with HCl the precipitate was centrifuged,filtered and dried. The product was then extracted with pyridine by shaking for 10 hours at room temperature.

4)^{1}H-NMR. ^{1}H-NMR was recorded in d-quinoline for quinoline extracts and in d-pyridine for pyridine extracts of NaOH-alcohol reaction products,using TMS as an internal standard. The concentration was 5% for d-quinoline and 2% for d-pyridine.

Results and Discussion

First the extraction conditions were examined using Indian Ridge coal and Balmer coal. The results are shown in Table 2. The effect of temperature from 350 to 375°C,of time from 1 hour

to 6 hours and of nitrogen pressure from 0.1 MPa to 10 MPa were examined. The results were in an error range and we adopted a rather higher temperature for older coals.

The extraction or reaction condition,extraction yield,ultimate analysis of extracts and their molecular weight are shown in Table 3. Quinoline extraction yield attains maxima in a range of 81~87 %C,but there is some scattering of results even with the same carbon percent. If we plot the extraction yield vs $\frac{H}{C}$ of raw coals a linear relationship was seen in a range of 91.5~81.2%C(Fig 1). In younger coals it decreases linearly. Teshio coal has an extraction yield of 20.4%,but after hydrolysis with NaOH solution (5N) at 250°C for 6 hours,the extraction yield increases to 35.9%. Therefore the ether linkages appear to be a cause of the decrease of extraction yield in the younger coal range. In the hydrolysis reaction associated with partial hydrogenation using NaOH-alcohol the younger the coals are,the easier the products dissolve in alcohol. This also means that the younger coals have an abundance of ether linkages.

The carbon percent of extracts in the younger coal range increases in comparison with that of raw coals. The quinoline extraction of NaOH-alcohol reaction conditions are somewhat severe for the younger coals and some oxygen containing functional groups such as carboxyl or hydroxyl groups decompose at those temperatures,which results in a reduction of oxygen content. In the higher coal rank the analytical values of extracts are nearly the same as those of the raw coals,although the extraction yield is higher, which means that there is no change in thier structure except for some splittings of ether linkages and a slight saturation of aromatic rings which took place in the reaction of NaOH-alcohol(3). In short,the unit structure(or structure of cluster unit)in the raw coals may be preserved without change in the quinoline extracts or in the pyridine extracts of NaOH-alcohol except for some changes of functional groups in the younger rank coals.

The results of the structural analysis are shown in Table 4. In bituminous coals in which the extraction yield of both methods is nearly 100%,the results show an amazing coincidence in both methods except for slightly higher values for fa,σal,Calus,although the methods are completely different. The higher values for these indices come from a slight hydrogenation in the NaOH-alcohol reaction. In the younger rank of coal the difference is somewhat higher,but in spite of this the coincidence is sufficient to discuss the rough unit structure,although the extraction yield and method are quite different. This small difference comes partly from the difference of extraction yield and partly from the slight hydrogenation of coal in NaOH-alcohol reaction.When we pursue the change of structural indices with time at 260°C for Taiheiyo coal in NaOH-alcohol reaction fa changes from 0.7 at 1 hour to 0.5 at 22hours. The extrapolated value of fa for 0 hour almost corresponds to that of the quinoline extract. The extrapolated value of Ra is 1.4 which also coincides well with 1.5 of quinoline extract. All other indices show the same coincidence. We have shown these extrapolated values in Table 4.

The results show that the aromatic ring number of the younger coals is 1~2 with 0.5naphthenic ring,that of 80~85%C coal 2~3 with 0.5 naphthene ring and that of 90%C coal 5 with 1 naphthene ring. The molecular weight per unit structure of younger coals is 160~180,that of 80~85%C coal 200~300 and that of 90%C coal 320~340.Oxygen content per unit structure decreases from younger coals

to the older coals,but as described before those values in younger coals do not represent the true ones. If we take the analytical values of raw coals,we can obtain the corrected oxygen number per unit structure,as shown in Table 4.

Refering to the fact that the ether linkages are rich in younger coals,we can say that the unit structures consisting of benzene or naphthalene rings with 0.5 naphthenic ring are linked mainly by the ether linkages and methylene bonds in younger coals. In bituminous coals the unit structure consisting of 2~5 aromatic rings and about 1 naphthene rings are linked with each other mostly by the methylene bonds. The youngest coal has 2.5~2.8 oxygen atoms per unit structure.The bituminous coals have about 1 oxygen atom per unit structure and the highest rank of coal has 0.3.

Appendix

Structural analysis. Hydrogen was divided into the following four types.Aromatic hydrogen Ha:6~9ppm,hydrogen attaching α carbon H_α: 2~5ppm,hydrogen attaching over β carbon except for terminal methyl H_β:1.1~2ppm,hydrogen in terminal methyl H_γ:0.3~1.1ppm. First 60% oxygen is assumed to be the hydroxyl group and the hydrogen in this hydroxyl group was subtracted from the total hydrogen. The residual hydrogen was distributed in the above four types.

The structural indices was calculated from the following equations when the molecular weight was not known.

$$\text{aromaticity, } fa=\frac{C/H-1/2\cdot(H_\alpha+H_\beta)/H-1/3\cdot(H_\gamma/H)}{C/H} \quad (1)^{4)}$$

H/C ratio in hypothetical unsubstituted aromatics,

$$Haus/Caus=\frac{Ha/H+1/2\cdot(H_\alpha/H)+0.6O/H+2\cdot(0.4O+N)/H}{C/H-1/2\cdot(H_\alpha+H_\beta)/H-1/3\cdot(H_\gamma/H)} \quad (2)^{4)}$$

$$\text{degree of substitution, } \sigma=\frac{1/2\cdot(H_\alpha/H)+0.6O/H+2\cdot(0.4O+N)/H}{Ha/H+1/2\cdot(H_\alpha/H)+0.6O/H+2\cdot(0.4O+N)/H} \quad (3)^{4)}$$

$$\text{degree of aliphatic substitution, } \sigma al=\frac{1/2\cdot(H_\alpha/H)}{Ha/H+1/2\cdot(H_\alpha/H)+0.6O/H+2\cdot(0.4O+N)/H} \quad (4)^{5)}$$

$$\text{number of aromatic carbon per unit structure, } Caus=\frac{3}{(Haus/Caus)-1/2} \quad (5)^{6)}$$

$$\text{number of total carbon per unit structure } Cus=Caus/fa \quad (6)$$

$$\text{number of aliphatic carbon per unit structure, } Calus=Cus-Caus \quad (7)$$

$$\text{number of hydrogen per unit structure, } Hus=12Cus\cdot H\%/C\% \quad (8)$$

$$\text{total ring number per unit structure, } Rtus=Cus-Hus/2-Caus/2 \quad (9)$$

$$\text{aromatic ring number per unit structure, } Raus=1/2\cdot(Caus-Haus)+1, \quad (Haus=(Haus/Caus)\cdot Caus) \quad (10)^{7)}$$

naphthenic ring number per unit structure, $Rnus = Rtus - Raus$ (11)

molecular weight per unit structure, $Mol.WT.us = 12\mathbb{C}us/C\%$ (12)

(5) is only valid for cata condensed aromatic nuclei. (9) is approximately valid when the degree of polymerization is large.

The absolute values of the number of each type of atoms were used when the molecular weight was known. In this case (9) was calculated as follows.

degree of polymerization $n = \mathbb{C}/\mathbb{C}us$ ($\mathbb{C}$ is the total number of carbon per molecule) (13)

total number of aromatic carbon per molecule, $\mathbb{C}a = \mathbb{C}aus \cdot n$ (14)

total ring number per molecule, $Rt = \mathbb{C} - \mathbb{H}/2 + 1 - \mathbb{C}a/2$, ($\mathbb{H}$ is total number of hydrogen per molecule) (15) [1]

total ring number per unit structure, $Rtus = Rt/n$. (16)

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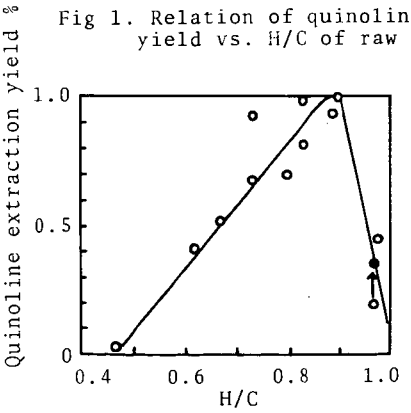
Fig 1. Relation of quinoline extraction yield vs. H/C of raw coals.



● Hydrolysis product

Table 1. Analysis of sample coals.

*S+O

No	Name	Ash %	ultimate analysis(daf) %				
			C	H	N	S	O_{diff}
1	Teshio	7.0	71.5	5.8	1.8	-	20.9*
2	Taiheiyo	5.3	77.9	6.3	1.1	0.2	14.5
3	Akabira	3.9	81.2	6.0	1.7	-	11.1*
4	Basewater	2.8	83.6	5.6	1.7	0.7	8.4
5	Miike	8.9	83.9	6.3	1.2	2.1	6.5
6	Daiyon	2.4	84.0	5.8	2.0	0.8	7.4
7	New Yubari	2.5	86.7	6.2	1.1	-	6.0*
8	Indian Ridge	1.5	87.4	5.3	0.9	-	6.4*
9	Goonyella	1.5	87.9	5.4	1.9	0.6	4.2
10	Balmer	2.5	89.4	5.0	1.4	0.4	3.9
11	Beatrice	0.8	91.5	4.7	1.3	0.6	1.9
12	Hongei	1.0	93.4	3.7	1.1	0.3	1.5

Table 2. Examination of quinoline extraction yield.

Coal	Indian Ridge				Balmer	
Temperature °C	350	360	370	375	380	380
Time hrs	4	6	1	1	4	4
Pressure MPa	5	0.1	10	0.1	1	10
Extraction yield %	63.0	64.0	61.5	68.0	51.9	50.0

Table 3. Extraction or reaction condition, yield, ultimate analysis and molecular weight of extracts.

No	Reaction[1]	Temperature°C	Time hr	Yield %	ultimate analysis %				molecular weight
					C	H	N	Odiff	
1	Q	350	4	35.9[2]	83.0	6.2	3.6	7.2	-
	N	300	1	97.8[3]	78.4	7.8	1.6	12.2	755
2	Q	350	4	44.9	82.9	7.0	2.1	8.0	-
	N	300	1	98.1[3]	80.8	8.1	1.3	9.8	870
3	Q	350	1	93.8	81.8	5.7	2.4	10.1	-
	N	300	1	96.9[3]	82.6	7.2	1.9	8.3	890
4	Q	350	4	69.0	83.6	5.5	2.2	8.7	-
5	Q	350	4	100.0	84.5	6.2	1.4	7.9	-
6	Q	350	4	81.0	82.7	5.8	2.9	8.6	-
7	Q	350	4	97.8	85.8	5.7	1.4	7.1	-
	N	350	1	91.1[3]	86.8	6.4	1.7	5.1	1160
8	Q	375	1	68.0	87.2	5.2	1.4	6.2	-
	N	350	1	52.4[3]	86.9	6.5	1.3	5.3	905
9	Q	350	4	93.0	86.7	5.2	3.8	4.3	-
10	Q	380	4	51.9	88.1	5.0	2.4	4.5	-
11	Q	370	4	41.6	88.8	4.9	1.7	4.6	-
12	Q	350	4	1.3	-	-	-	-	-

1)Q:quinoline extraction, N:NaOH-alcohol reaction,pyridine extracts.
2)Hydrolysis product with NaOH solution at 200°C,6hrs.
3)Pyridine extraction yield of NaOH-alcohol reaction products.

Table 4. Results of structural analysis.

No	1		2			3		4	5
Reaction[1]	Q	N	Q	N	N'5)	Q	N	Q	Q
Ha%	0.38	0.11	0.37	0.13	-	0.43	0.22	0.51	0.37
Hα%	0.28	0.36	0.25	0.35	-	0.34	0.39	0.29	0.32
Hβ%	0.27	0.41	0.32	0.41	-	0.16	0.29	0.16	0.25
Hγ%	0.06	0.12	0.06	0.10	-	0.08	0.10	0.05	0.06
fa	0.75	0.53	0.71	0.52	0.70	0.79	0.63	0.82	0.75
Haus/Caus	0.82	1.00	0.88	0.97	0.90	0.81	0.89	0.78	0.75
σ	0.47	0.77	0.43	0.65	0.45	0.48	0.54	0.41	0.46
σal	0.20	0.39	0.20	0.40	0.17	0.20	0.34	0.17	0.23
Cus	12.5	11.5	11.1	12.3	11.5	12.3	12.4	13.1	16.0
Caus	9.4	6.0	7.9	6.4	8.0	9.7	7.7	10.7	12.0
Calus	3.1	5.5	3.2	5.9	3.4	2.6	4.6	2.4	4.0
Rtus	2.3	1.9	1.6	1.9	1.8	2.3	2.3	2.5	3.1
Raus	1.8	1.1	1.5	1.1	1.4	1.9	1.4	2.2	2.5
Rnus	0.5	0.9	0.1	0.8	0.4	0.4	0.8	0.4	0.6
Mol.Wtus[2]	181	176	161	183	181	180	180	188	227
Ous[3]	0.8	1.4	0.8	1.1	2.0	1.1	0.9	1.0	1.1
Ous'[4]	2.8	2.5	1.6	1.7	-	-	-	-	-

No	6	7		8		9	10	11
Reaction[1]	Q	Q	N	Q	N	Q	Q	Q
Ha%	0.39	0.39	0.26	0.52	0.28	0.48	0.55	0.63
Hα%	0.29	0.28	0.29	0.26	0.36	0.31	0.27	0.24
Hβ%	0.25	0.25	0.27	0.16	0.27	0.15	0.15	0.09
Hγ%	0.06	0.08	0.11	0.05	0.09	0.06	0.02	0.04
fa	0.77	0.80	0.70	0.84	0.70	0.83	0.86	0.89
Haus/Caus	0.76	0.66	0.67	0.65	0.69	0.68	0.64	0.64
σ	0.48	0.43	0.53	0.35	0.45	0.42	0.35	0.29
σal	0.20	0.20	0.33	0.16	0.32	0.19	0.16	0.14
Cus	15.0	23.4	25.7	23.8	22.2	20.1	24.9	24.1
Caus	11.5	18.8	17.6	20.0	15.8	16.7	21.4	21.4
Calus	3.5	4.6	7.7	3.8	6.6	3.4	3.5	2.7
Rtus	3.0	4.8	5.7	5.3	4.9	4.6	5.9	5.4
Raus	2.4	4.2	4.0	4.5	3.4	3.7	4.9	4.9
Rnus	0.6	0.6	1.8	0.8	1.5	0.9	1.0	0.5
Mol.Wtus[2]	218	328	356	328	307	279	340	326
Ous[3]	1.2	1.5	1.1	1.3	1.0	0.1	0.4	0.3
Ous'[4]	-	-	-	-	-	-	-	-

1)Q:quinoline extraction
N:NaOH-alcohol reaction
2)Molecular weight per unit structure
3)Number of (oxygen atom)diff. per unit structure
4)Corrected number of (oxygen atom)diff. per unit structure
5)Extrapolated values to 0 hour in the time variation reaction at 260°C.